Loss of Ag and Cl from Photochromic Glasses during Melting in Various Atmospheres

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The processes of loss of Ag and Cl from photochromic glass batches during melting has been investigated. They were classified into three due to liquid phase separation, vaporization of chlorides from the glass melts and oxidation of chlorides by air. Effects of presence of chloride vapors in the melting atmosphere on the amounts of Ag and Cl remained in the glasses were also examined. When melted in the atmosphere saturated with AgCl, the Ag content of the glass increased rapidly with time, whereas its Cl content remained unchanged.

I. INTRODUCTION

Silver halides in photochromic glasses tend to vaporize during melting, and hence massproduction of these glasses containing a constant amount of silver halides is difficult. In the present work, the processes of escape of silver and halogen from photochromic glass batches during melting have been investigated. The glass melting was made in the air as well as in the air saturated with AgCl, NaCl, or $BaCl_2$ vapor.

Dissolution of silver into molten glasses in the presence of oxygen has been reported in many literatures. Recently, Willis[1] and Maekawa[2] have reported that the solubility of silver into a molten borate glass increased as an oxygen partial pressure of the furnace atmosphere increased. However, there has been no systematic study on the solubility of silver in molten glasses in the atmosphere containing halogens.

II. EXPERIMENTAL

II.1 Glass Batches

Compositions of the glass batches prepared are given in Table 1. AgCl glass 1, 2, and 3 denote the glasses containing various amounts of AgCl. Their base batch compositions are the same. Batch compositions of NaCl glass and $BaCl_2$ glass are the same as that of AgCl glass 1, except the contents of the sodium and barium compounds, *i.e.*, in the former all of the Na_2CO_3 are substituted by the equimole NaCl and in the latter a part of the $BaCO_3$ is substituted by the equimole $BaCl_2$, both for increasing the Cl content of the resultant glasses. An oxide composition given in Table 2 was calculated from the batch composition of AgCl glass 1. This is similar to those of typical photochromic glasses in literatures.[3]

II.2 Apparatus for Glass Melting

An apparatus for melting the glasses in the air saturated with chloride vapor is sche-

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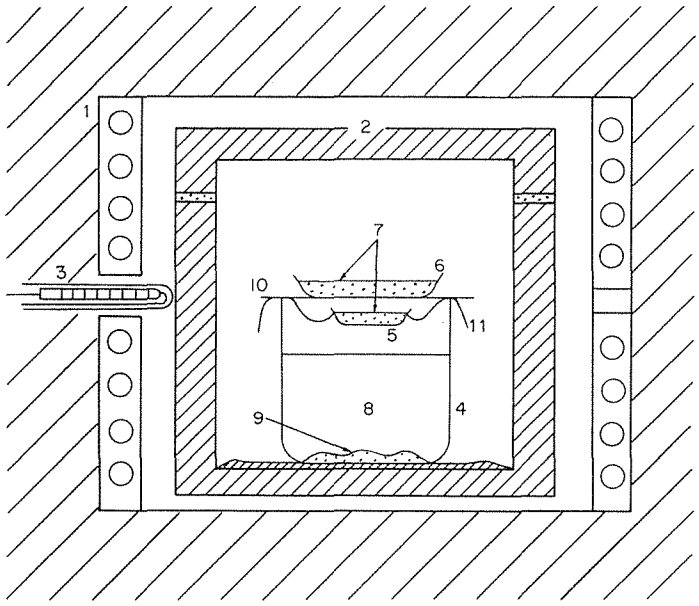

1 Electric resistance furnace
2 Refratory crucible (150 cc)
3 Thermocouple
4 Alumina crucible (50 cc)
5, 6 Platinum bowls
7 AgCl, NaCl or $BaCl_2$ melt
8 Glass
9 Phase-separated chloride (AgCl)
10 Platinum lid
11 Platinum wire

Fig. 1. Apparatus for glass melting

matically shown in Fig. 1. The glass batch was charged in a sintered alumina crucible of 50 cc in capacity (4), on which a platinum lid (10) was placed. The alumina crucible was placed in a refractory crucible of 150 cc in capacity with a refractory lid (2). Between the refractory crucible and lid glass powders were placed to improve gastightness. In order to fill a chloride (AgCl, NaCl or $BaCl_2$) gas in the alumina crucible a small bowl

Table 1. Batch Composition

	AgCl glass			NaCl glass	$BaCl_2$ glass
	1	2	3		
SiO_2	40.0 g	40.0 g	40.0 g	40.0 g	40.0 g
H_3BO_3	27.1	27.1	27.1	27.1	27.1
$Al(OH)_3$	8.01	8.01	8.01	8.01	8.01
Li_2CO_3	4.90	4.90	4.90	4.90	4.90
Na_2CO_3	2.34	2.34	2.34	—	2.34
NaCl	—	—	—	2.59	—
$BaCO_3$	8.01	8.01	8.01	8.01	3.65
$BaCl_2$	—	—	—	—	4.63
PbO	3.66	3.66	3.66	3.66	3.66
ZrO_2	1.60	1.60	1.60	1.60	1.60
Cu_2O	0.011	0.011	0.011	0.011	0.011
AgCl	0.45	3.15	6.31	0.45	0.45
Total	96.08	98.78	101.94	96.33	96.35

Table 2. Glass Composition

SiO_2	52.63 wt. %
B_2O_3	20.09
Al_2O_3	6.89
Li_2O	2.90
Na_2O	1.80
BaO	8.18
PbO	4.81
ZrO_2	2.10
Cu_2O	0.014
Ag	0.44
Cl	0.15
Total	100.00

filled with chloride powders (5) was hung by three platinum wires from the upper edge of the crucible. To suppress penetration of air from the outside of the alumina crucible a larger platinum bowl filled with chloride powders (6) was also placed on the platinum lid (10). Vapor pressures at 1400°~1500°C of the chlorides used in the present experiments are given in Table 3 for reference.[4] The glass melting in the air atmosphere was performed in the same way as described above but without placing the powders in the two platinum bowls. Unless specially noted the glass melting was made at 1400°C for 3 hours after the batch charge which took about one hour.

II.3 Determination of Ag and Cl Contents in Glasses

The amounts of Ag and Cl remaining in the glasses after melting were measured by X-ray fluorescence analyses. The pulse height analyser and the germanium spectroscopic crystal for cutting off 2nd order X rays were used because the contents of Ag and Cl in all the glasses were so small (both mostly less than 0.5 wt.%) that their analyses were difficult.

III. RESULT

III.1 AgCl Glass 1, 2, 3

Figure 2 shows the analytical results of the Ag and Cl contents in AgCl glass, 1, 2, and 3 (ref. Table 1) melted respectively for 1, 2.5 and 4 hours from the beginning of their batch charges. All of the batches were charged in the air atmosphere within the melting time from 0 to 1 hour and thereafter their melting was continued in the air or in the air saturated with AgCl vapor produced by the method described above. In the crucibles allowed to cool to room temperature, in which AgCl glass 2 and 3 were melted, a crystalline phase was found to separate from the glass phase, forming a mass in the bottom of the crucible as shown in Fig. 1. Figure 3 (a) shows an X-ray diffraction pattern of the crystalline phase separated from AgCl glass 3 melted for 4 hours in the air saturated with AgCl vapor. Chemical analysis showed that it was composed of 96.4 wt.% AgCl and 2.6 wt.% residue insoluble to 6*N* NH_4OH and conc. HCl solutions. Figure 4(a) shows changes in amount of the crystalline phase separated from the glass with the melting time.

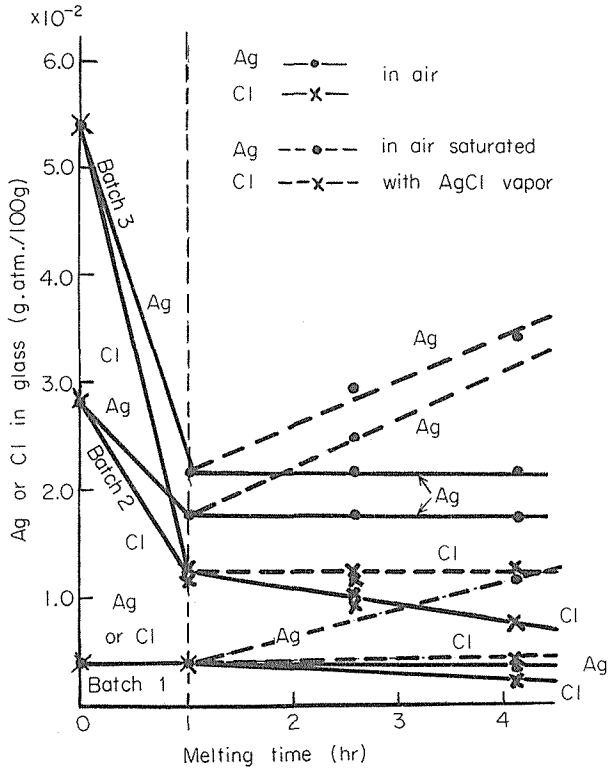

Fig. 2. Concentrations of Ag and Cl in the glasses melted at 1400°C in various atmospheres.

III.2 NaCl and $BaCl_2$ Glass

Figure 5 shows the changes in contents of Ag and Cl in NaCl and $BaCl_2$ glass with the melting time. In these experiments, too, their batches were charged in the crucibles in the air atmosphere within the melting time from 0 to 1 hour. Thereafter, their melting was continued in the air saturated with NaCl or $BaCl_2$. As the changes in Ag content were small, they were magnified in Fig. 6. In the crucible allowed to cool to room temperature, in which NaCl glass was melted in the air saturated with NaCl vapor over 2.5 hours, a crystalline phase was found to separate from the glass phase, forming a thin layer about 0.7 mm thick (0.5~0.6 g) over the glass phase. Chemical analysis showed that the crystalline material, separated from the glass melted in the air saturated with NaCl vapor for 4 hours, was composed of 68.6 $BaCl_2$, 25.8 NaCl, 3.0 AgCl and 2.6 wt.% residue insoluble to conc. HCl and 6*N* NH_4OH solutions. Its X-ray diffraction pattern is shown in Fig. 3 (b). No Pb was detected in this crystalline material by the X-ray fluorescence analysis. Figure 4(b) shows the change in the amount of the crystalline material separated from the NaCl glass phase with the melting time. In the cases when $BaCl_2$ glass was melted in the air saturated with $BaCl_2$ vapor, and also $BaCl_2$ glass or NaCl glass was melted in air, no separation of the crystalline phase occurred.

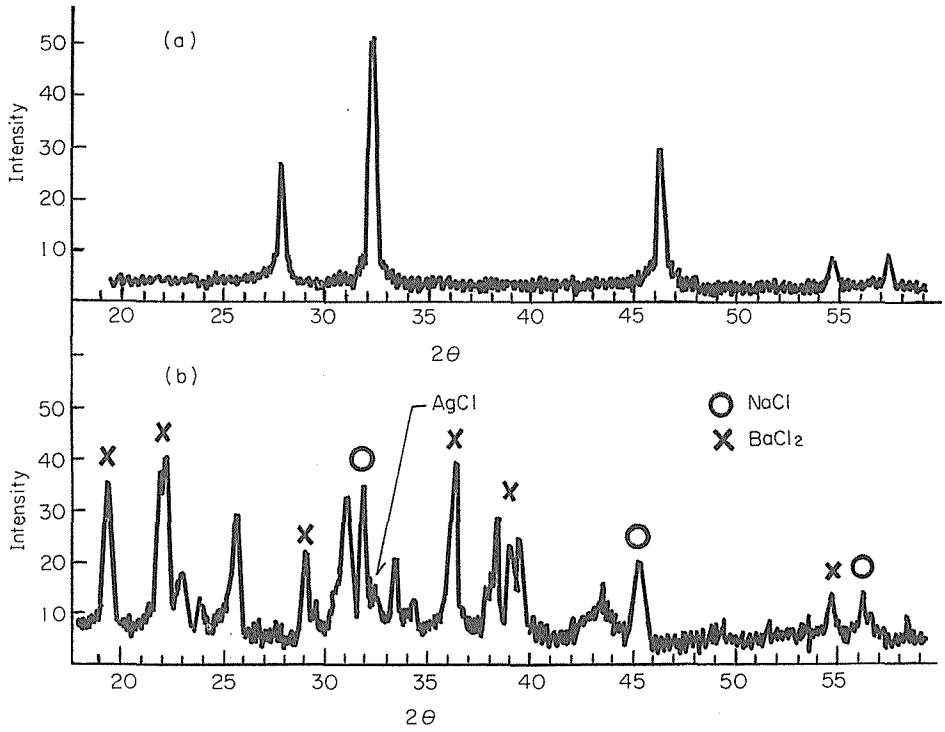

Fig. 3. X-ray diffraction diagrams of
(a) chlorides phase-separated from AgCl glass 3 melted in air saturated with AgCl vapor,
(b) chlorides phase-separated from NaCl glass melted in air saturated with NaCl vapor.

III.3 Effects of Melting Time and Melting Temperature

Figure 7 shows the changes, with the melting time, of Ag and Cl contents in the $BaCl_2$ glass melted in the air for a long time. The melting temperature was 1450°C. Throughout a run, the lids of alumina and refractory crucible were left open so that fresh air came freely to the surface of the glass melt, and moreover the melt was stirred every 1.5 hours for its homogenization with a quartz glass rod of 7 mm in diameter. As the measured values of the Cl contents fairy scattered, their dispersion limits are shown with arrows in Fig. 7. The rate of decrease in the Cl content was about ten times greater than that of the Ag content. The decreasing rates of their contents during melting were similar to that in the glass melted without stirring (Fig. 5). As the melting temperature differs a little in each case, the results can not be compared, but apparently the stirring of the glass has not a particular effect accelerating the vaporization of Ag and Cl.

Figure 8 shows effects of melting temperature on the Ag and Cl contents for the $BaCl_2$ glass melted for 6 hours. The melting conditions were the same as those in the previous experiment. It can be seen from the figure that the Cl content decreases much more markedly than the Ag content as the melting temperature increases; the decrease of the Cl content per 100°C was 4.6×10^{-3} g.atm. per 100 g glass whereas that of the Ag content was 0.30×10^{-3} g.atm. per 100 g glass.

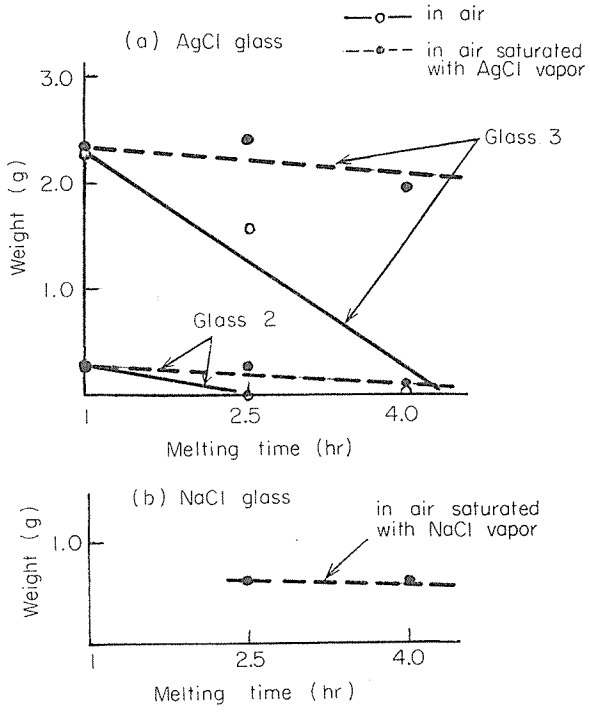

Fig. 4. Decrease in weight of chlorides phase-separated from (a) AgCl glass and (b) NaCl glass melted in various atmospheres.

IV DISCUSSION

IV.1 Two Liquid Phase Separation

In the systems consisting of halides there are many which contain a two liquid immiscibility region. The systems of CaF_2-SiO_2-CaO[5] and NaCl-TiO_2-Na_2TiO_3[6] are the examples. Although a phase diagram of the AgCl-Silicate system has not yet been published, separation of the chloride-rich phases from the batches containing large amount of AgCl or NaCl as observed in the present experiments would also have been caused by this two liquid immiscibility. Figure 9 shows a model of a phase diagram of the AgCl–Silicate system proposed by the authors. The compositions denoted by 2 and 3 in Fig. 9 correspond respectively to the compositions of AgCl glass 2 and 3. At 1400°C, both of them separate into two liquid phases, *i.e.*, a silicate-rich phase A and a AgCl-rich phase B, although the ratios in amount of their two phases are different. During melting of AgCl glass 2 or 3 at 1400°C in the air, AgCl will vaporize from the silicate-rich phase A, but its AgCl content will never change as long as the AgCl rich phase B coexists, since the AgCl lost from the silicate-rich phase will be replenished from the AgCl-rich phase. The melt of the composition A is saturated with AgCl at 1400°C and therefore in the melts containing more than this amount of AgCl the two liquid phase separation will occur as described above. The melts containing less than this amount of AgCl are unsaturated with AgCl. The composition denoted by 1 in Fig. 9 corresponds to one of these unsaturated

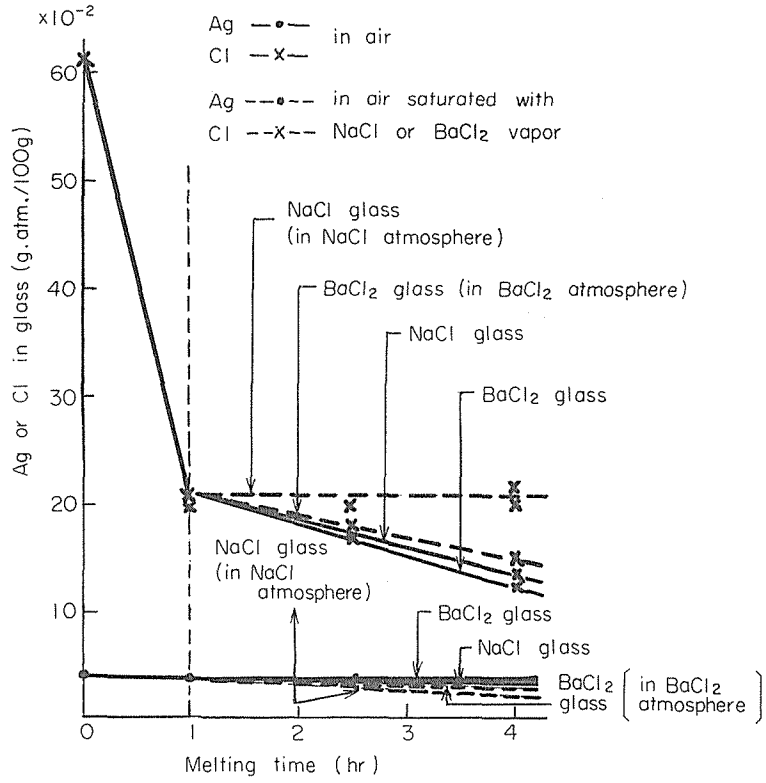

Fig. 5. Concentrations of Ag and Cl in the glasses melted at 1400°C in various atmospheres.

melts. If this melt be super-cooled through the liquidus temperature D to room temperature and again heated to the annealing temperature, for example, to 550°C and kept there for a long time, it will separate into the two compositions, F and E, which lie on the liquid immiscibility line extending below the liquidus. This process is a so-called two liquid phase separation, and through this process photochromic glasses containing numerous minute and well dispersed particles of AgCl crystals would be produced.

Table 3. Some Properties of Chloride

Chloride	M. P. (°C)	B. P. (°C)	Vapor pressure (mmHg)		
			1400°C	1450°C	1500°C
AgCl	455	1550	235	400	575
NaCl	800	1465	475	670	—
$BaCl_2$	963	1560	73	160	302

M. P. (*Melting point*), B. P. (*Boiling point*)

IV.2 Causes for Loss of Ag and Cl

Losses of Ag and Cl from the glass batches during melting are considered to occur

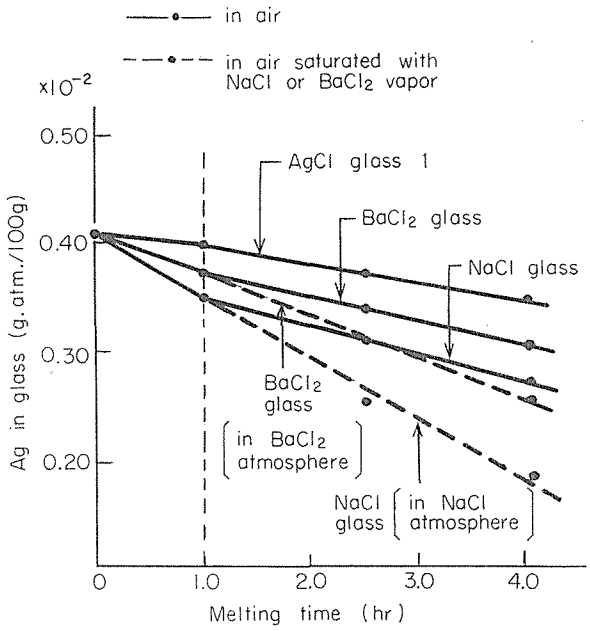

Fig. 6. Concentrations of Ag in the glasses melted at 1400°C in various atmospheres.

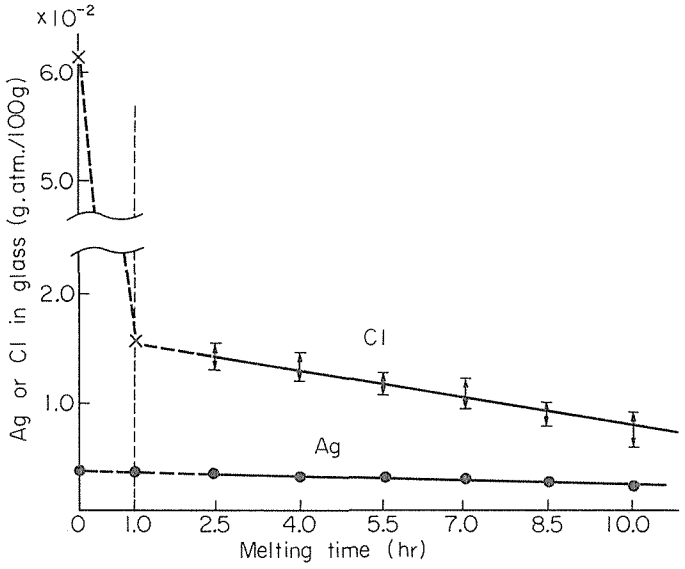

Fig. 7. Concentrations of Ag and Cl in $BaCl_2$ glasses melted at 1450°C in air for various times. The glasses were stirred intermittently every one and a half hour after completion of batch charge, *i.e.*, after one hour.

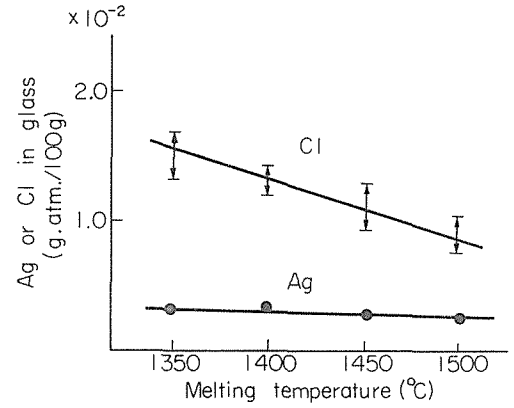

Fig. 8. Concentrations of Ag and Cl in $BaCl_2$ glasses melted at various temperatures for 6 hours after completion of batch charge. The glasses were stirred intermittently every one and a half hour during melting.

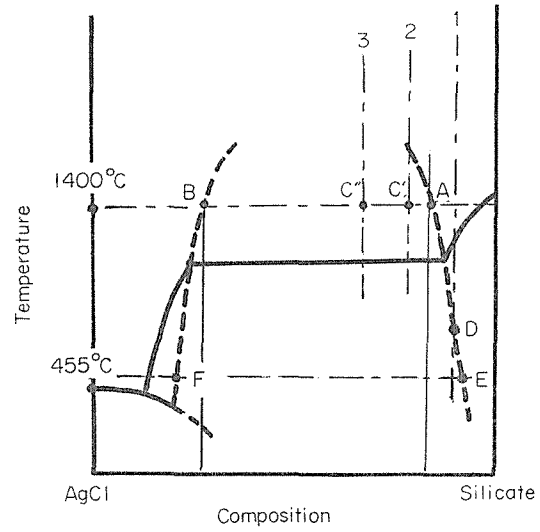

Fig. 9. Model of phase diagram of the AgCl-Silicate system.

mainly by the following three causes.

1) Separation of chloride-rich phase from the glass melt by two liquid phase separation.

2) Vaporization from the glass melt in the form of AgCl and NaCl *etc.* having high vapor pressure (ref. Table 3).

3) Oxidation of the chlorides represented by the following formula.

$$4AgCl+O_2 \longrightarrow 2Ag_2O+2Cl_2 \uparrow$$

By this reaction, only the Cl_2 is lost from the glass melt because the Ag_2O formed can dissolved into the glass melt because of its high solubility in the melt.[2,7] The oxidation of the chlorides in the glass melt must be taken in account, because, in the present experi-

ments, air can diffuse from outside into the refractory crucible through its wall or the gap between the crucible and the lid.

IV.3.1 Losses during Batch Charge (0–1 hour)

AgCl glass 2 and 3 containing large amounts of AgCl lost a large percentage of Ag and Cl during their batch charge (0∼1 hour) in the air atmosphere. The losses of Ag and Cl during the batch charge are ascribed to a series of the three processes described above. Table 4 gives total amounts of their losses from the glass phase as well as their details classified to their causes. The amount of AgCl transported into the AgCl rich-phase by the two liquid phase separation was caluculated from both of the results shown in Fig. 2 and of the chemical analysis of the AgCl rich-phase. The losses of Ag and Cl caused by vaporization in the form of AgCl were caluculated from the decrease of the AgCl content of the glass phase. The residual losses were regarded as caused by vaporization of the chlorides such as NaCl and $BaCl_2$ *etc.* According to the data shown in Table 4, the losses of Ag and Cl due to the separation of the AgCl rich-phase form a large percentage of their total losses especially for the glasses, such as AgCl glass 3 containing large amounts of AgCl. As the contents of AgCl in the glass batches decrease, the percentages of the losses of Ag and Cl from their glasses due to the vaporization of AgCl during melting increase. For AgCl glass 1 in which no two liquid phase separation occurred, the losses of Ag and Cl due to the vaporization of the chlorides and also to the oxidation of the chlorides during batch charge were all negligiblly small, *i.e.*, within experimental errors.

IV.3.2 Losses during Glass Melting after Batch Charge (1–4 hour)

The rates of the losses of Ag and Cl from the glasses during melting after batch charge were much smaller than those during the batch charge, since the excess amounts of AgCl in the glasses were already transferred to the chlorides-rich phase and the remaining AgCl almost completely dissolved in the silicate glass phase. In this period, the loss rates of Cl were generally higher than those of Ag, because Ag vaporized only in the form of AgCl, whereas Cl was able to vaporize in various forms of chlorides such as NaCl *etc.* and also in the form of Cl_2 produced as the result of the oxidation of the chlorides.

Table 4. Amounts of Ag and Cl lost from the Glass Batches during their Charge

Glass batch	Losses of Ag and Cl (g. atm./100 g oxide glass)			
	Total loss ($\times 10^2$)	By liquid phase separation ($\times 10^2$)	By vaporization of AgCl ($\times 10^2$)	By vaporization and oxidation* ($\times 10^2$)
AgCl glass 1	Ag 0.02 (<5%)** Cl 0.02 (<5%)	0 0	<0.02 (<5%) <0.02 (<5%)	<0.02 (<5%) <0.02 (<5%)
AgCl glass 2	Ag 1.05 (38%) Cl 1.60 (57%)	0.27 (9%) 0.27 (9%)	0.78 (29%) 0.78 (29%)	0 0.55 (19%)
AgCl glass 3	Ag 3.21 (59%) Cl 4.21 (78%)	2.0 (37%) 2.0 (37%)	1.2 (22%) 1.2 (22%)	0 1.0 (19%)

* by vaporization of chlorides except AgCl and oxidation of chlorides including AgCl

** Figures in parentheses represent wt.% of Ag and Cl losses respectively to their initial contents in the glasses.

IV.4 Losses of Ag and Cl from AgCl Glass 1, 2 and 3 during Melting in AgCl Atmosphere (Fig. 2)

The Ag contents in all of AgCl glass 1, 2 and 3 increased rapidly when the glasses were melted in the air saturated with AgCl vapor after their batch charges, whereas their Cl contents remained unchanged. The increase of the Ag contents can not be attributed to the dissolution of the AgCl vapor into the silicate glass phase because, for the AgCl glass 2 and 3, the glass phases were already saturated with AgCl, and hence it would have been due to dissolution of the Ag_2O produced by a reaction of the AgCl vapor and oxygen present in air having diffused into the platinum crucible from the outside. For AgCl glass 1, dissolution of the AgCl vapor into the glass melt would be possible until the saturation limit of AgCl as indicated by A in Fig. 9, but thereafter the dissolution of Ag in the form of Ag_2O would only be possible. High solubility of Ag_2O in the glasses has already been confirmed by Boulos and Kreidle,[7] for example, for the borate and silicate glasses.

IV.5 Losses of Ag and Cl from NaCl Glass or $BaCl_2$ Glass during Melting in NaCl or $BaCl_2$ Atmosphere (Fig. 4, 5 and 6)

The Cl content in NaCl glass was kept constant during the melting in the air saturated with NaCl vapor after the batch charge. This may be explained in the same way as in the case of melting of AgCl glass 2 and 3 in the air saturated with AgCl: The silicate-rich glass phase separating from the NaCl-rich phase was already saturated with NaCl and hence NaCl vapor was unable to dissolve into the glass phase. Although changes of the Na content in the glass phase were not measured, its content probably increased by dissolution of Na_2O produced by a reaction of the NaCl vapor with oxygen having diffused in the platinum crucible from the outside.

When the melting of NaCl glass was continued in air after the batch charge, the amount of the chloride-rich phase separated as well as the content of Cl dissolved in the silicate-rich phase (glass melt) decreased rapidly with time. The both results can be explained as the results of vaporization of NaCl and also of oxidation of NaCl by air.

Decrease of the Ag content in NaCl glass melted in air was smaller than that melted in the air saturated with NaCl (Fig. 6). This is probably due to the oxidation of AgCl by air; when melted in air, Ag_2O produced by oxidation of AgCl by air dissolves in the glass melt and thus escape of AgCl from the melt in the form of AgCl vapor is suppressed, whereas the air saturated with NaCl vapor is poor in oxygen and therefore the above effect is hardly produced.

The effects of the air saturated with $BaCl_2$ on the losses of Ag and Cl were intermediate between the air and the air saturated with NaCl. This may be explained by the larger content of the air in the atmosphere saturated with $BaCl_2$ than that of the atmosphere saturated with NaCl, because $BaCl_2$ has a lower vapor pressure than that of NaCl (Table 3).

V. SUMMARY

Batches of photochromic glasses (about 100 g) containing various amounts of Ag and Cl (the nominal oxide compositions; SiO_2 52.63, B_2O_3 20.09, Al_2O_3 6.89, Li_2O 2.90, Na_2O 1.80, BaO 8.18, PbO 4.81, ZrO_2 2.10, Cu_2O 0.014, Ag 0.44～5.80, Cl 0.15～2.18

wt.%) were melted at 1400° or 1450°C in the air or in the air saturated with AgCl, NaCl or $BaCl_2$ vapor and the amounts of Ag and Cl remaining in the glasses after melting for various times were measured by X-ray fluorescence analyses. The results were summarized as follows.

Losses of Ag and Cl from the glasses in the melting process were considered to occur mainly by the following three causes. 1) separation of chloride-rich phase from the glass melts by two liquid phase separation. 2) Vaporization from the glass melts in the form of AgCl, NaCl, *etc.* having the high vapor pressure. 3) Oxidation of chlorides represented by the following formula.

$$4AgCl+O_2 \longrightarrow 2Ag_2O+2Cl_2 \uparrow$$

In this reaction, only the Cl_2 is lost from the glass melts because the Ag_2O formed has high solubility in the glass melts.

When the glasses were melted in the air saturated with the AgCl vapor, the Ag contents increased rapidly, whereas the Cl contents were held constant. When the glasses were melted in the air saturated with NaCl vapor, the Ag contents decreased at slow rates, whereas the Cl contents were held constant. The loss rate of the Ag in the air saturated with NaCl vapor was higher than in the air. Effects of the air atmosphere saturated with $BaCl_2$ vapor were intermediate between those in the air and in the air saturated with the NaCl vapor. The above results were explained by suppressing effects of the chloride vapors in the atmosphere on vaporization of the chlorides from the molten glasses and also on oxidation of the chloride vapors by the air.

Mechanical stirring of the molten glass did not give remarkable effects in accelerating vaporization of the chlorides from the molten glasses.

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